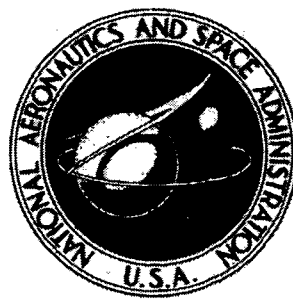


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**PREPARATION OF THIN FILM
SILVER FLUORIDE ELECTRODES
FROM CONSTITUENT ELEMENTS**

by Patricia M. O'Donnell

Lewis Research Center

Cleveland, Ohio 44135

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16. Abstract The feasibility of preparing thin-film metal fluoride electrodes from the elemental constituents has been demonstrated. Silver fluoride cathodes were prepared by deposition of silver on a conducting graphite substrate followed by fluorination under controlled conditions using elemental fluorine. The resulting electrodes were of high purity, and the variables such as size, shape, and thickness were easily controlled.					
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PREPARATION OF THIN FILM SILVER FLUORIDE ELECTRODES FROM CONSTITUENT ELEMENTS

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SUMMARY

This report describes a method of electrode preparation from constituent elements to produce a well characterized electrode suitable for electrochemical studies. The silver fluoride electrodes were prepared by the deposition of silver on a graphite substrate by three methods: electrodeposition, pasting, and vapor deposition. The silver films were then reacted with fluorine gas to form a silver fluoride electrode. Electrochemical measurements showed that this method produced an electrode which could be discharged efficiently.

INTRODUCTION

Work in the area of nonaqueous-electrolyte high energy-density batteries has demonstrated a need for well characterized electrodes to use in these systems. The search for a high energy-density power source has revealed many problems (ref. 1). The high energy-density battery must use a high-purity nonaqueous electrolyte and electrodes that are well characterized. Inorganic fluorides are promising cathode materials with theoretical energy densities greater than 3.9 watt-seconds per kilogram (500 W-hr/lb) when used in combination with a lithium electrode. There are several methods in the literature (refs. 2 to 5) for making inorganic electrodes, however, they all involve procedures that contribute to the unknown character of the final product. Such procedures are high pressure pelletizing, mixing the desired material with a binder, pasting reactants on to metal grids, or filtration to form an electrode cake on a support. It would be desirable to fabricate well characterized thin-film inorganic electrodes on a conducting substrate by a simple direct method. As an approach to this problem thin-film silver fluoride electrodes have been prepared on a graphite substrate starting from elemental silver and fluorine.

EXPERIMENTAL

Substrate

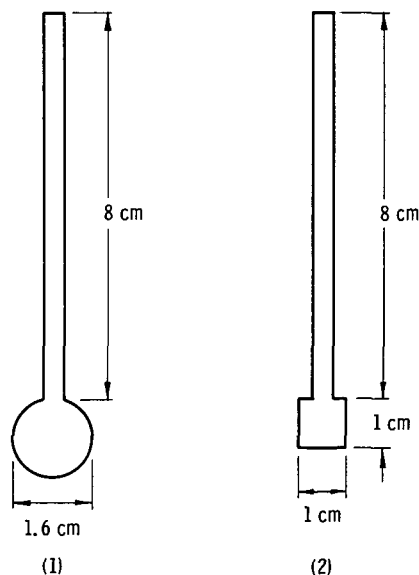
The three forms of graphite substrate used in this experiment are described in table I along with the effects of fluorine exposure on them. The apparatus used in this study is fully described in reference 6 and is shown in figure 1.

The graphite samples were weighed and inserted in the furnace in an alundum boat. Surface characteristics were observed microscopically. Most of the work was concentrated on the graphite sheet substrate because of the ease of handling and the convenience of being able to cut the electrodes into any desired shape.

Silver Coating

A thin layer of silver was deposited on the selected substrate. Three deposition methods were investigated: electrodeposition, pasting, and vapor deposition.

Electrodeposition. - A silver cyanide bath (Dalic process) was used at 25°C (298 K) at a current density of 62.5 amperes per square meter (5.8 A/ft^2) to electrodeposit the silver in thicknesses from 5 to 88 micrometers (0.2 to 3.5 mils). Unreacted silver was a problem with the thickest films, and adhesion was a problem with the very thin film. An optimum thickness was about 25 micrometers (1 mil). The most desirable substrate shape for the electrodeposition turned out to be a lollipop configuration either round (1) or squared (2) as shown in sketch (a):



(a)

The graphite was degreased with trichloroethylene before electroplating. After plating, the sample was heated in the vacuum oven at 225⁰ C (498 K) to drive off any alkyl amines or organic acids that could have been picked up from the plating solution. The electrodeposited silver was white because of the small crystallite size.

Pasting. - A suspension of silver in butyl acetate (DuPont) was used to put a thin film of silver on the graphite using a brush. There is little control of the thickness using this method. A simple vacuum treatment without heat was used to pump off the solvent.

Vapor deposition. - Clean graphite foil substrates were put into a commercial vacuum deposition apparatus. A very uniform layer of silver was electron beam evaporated from a tantalum container onto the graphite substrate which was rotated 43 centimeters (17 in.) from the source. The pressure was 10⁻⁴ newtons per square meter (10⁻⁶ torr) during evaporation. As will be discussed later, these samples exhibited the best properties. The silver deposit was 25 micrometers (1 mil) thick.

Reaction with Fluorine

The silver film on the graphite substrate must be converted to an electrochemically active material. This was done by reacting it with 39.9 kilonewton per square meter (300 torr) fluorine at temperatures up to 250⁰ C (523 K) (ref. 6). The desirable product from an electrochemical point of view is the difluoride because of its higher theoretical energy density. A Monel sample holder as shown in figure 2 was used rather than an alundum boat to expose the foil samples uniformly to fluorine. It had the added advantage that four electrodes could be reacted at the same time if one so desired.

The reacted films nonadherence to the substrate in the form of beads was a problem. It was determined that this was not inherent in the silver films but only occurred when the film was reacted with fluorine. Several procedures were tried in order to eliminate this beading, and the following combination of parameters gave good results:

- (1) The sample was preheated under vacuum for 0.5 hour at 300⁰ C (573 K).
- (2) The heaters were turned off and the sample was allowed to cool under vacuum.
- (3) Fluorine was introduced into the cool furnace.
- (4) The temperature was brought up to 250⁰ C (523 K).
- (5) Reaction was continued for 3 hours.

Electrochemical Measurements

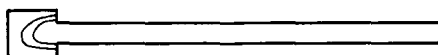
Electrochemical studies of the silver fluoride films were carried out in saturated potassium hexafluorophosphate-propylene carbonate (KPF₆-PC) electrolyte. Careful

purification of the materials was necessary because it was determined that the electrode stability varied directly with the water content. The PC was dried by passing it through a molecular sieve, then it was vacuum distilled. The conductivity of the propylene carbonate was 0.3×10^{-7} per ohm per centimeter indicating a water content of < 50 ppm (ref. 7). The salt was recrystallized from alkaline aqueous solution, thoroughly dried at 110° C in a vacuum oven, and assayed at 99 percent. The KPF_6 saturated electrolyte had a conductivity of 5.3×10^{-3} per ohm per centimeter.

Measurements were done chronopotentiometrically using the cell shown in figure 3. The silver fluoride electrode was discharged with a platinum coil as the counter electrode and a Ag/Ag^+ electrode as the reference. The cell was operated in a dry box under argon, and all manipulations were performed in the dry box. Using an electronic potentiostat wired for galvanostatic operation, the discharge current was held constant, and the variation in voltage was followed on a recorder as a function of time.

RESULTS AND DISCUSSION

All the fluorinated samples were similar in appearance on removal from the furnace. However, on standing, in the absence of light to eliminate any photochemical effect and sealed under argon, the electrodeposited samples developed unusual but reproducible colored rings as shown below. It was believed that this was due to a variation in the composition of the film. (See sketch (b).)



(b)

X-ray analysis of the different areas supported this view since the monofluoride and subfluoride were identified along with the difluoride. A variation in the silver film thickness originally deposited could possibly account for the additional silver compounds found.

If this is the case a film of very uniform thickness should not show this effect. Using the vapor deposition technique mentioned earlier, silver films of very uniform thicknesses were laid down. These films were fluorinated under the same conditions as the electrodeposited films. As expected, the product obtained with the vapor deposited films was stable with time in dry argon in the dark and exhibited no ring formation.

A typical electrochemical discharge curve is shown in figure 4 for the 3.2-

milliampere-per-square-centimeter experiment. The discharge is very flat as were the experiments at 10 and 25 milliamperes per square centimeter, and no indication of a two-step discharge was observed. A single plateau discharge has also been reported by Shaw (ref. 5) on uncycled cells. These data can be used to determine the number of coulombs available in the silver fluoride film that are electrochemically active. Comparison with the total amount of silver difluoride formed, obtained by weight gain measurements after fluorination enables a discharge efficiency to be calculated. The electrode was discharged until a sudden change in voltage occurred. The discharge efficiency results are summarized in table II. It should be noted that since the efficiencies are greater than 50 percent in all cases, the single plateau discharge cannot be attributed to a lower oxidation state material.

The mechanical integrity of the electrode was lost at the same time as the sudden change in voltage occurred. Once the film was discharged from the surface, the graphite expanded destructively. This is possibly due to discharge of potassium and reaction with the graphite (ref. 8). No attempts were made to recharge. The infrared spectra before and after discharge suggests that the electrolyte remained essentially unchanged. However, a change in the color was observed, and the electrolyte in the working side became more acidic than that in the counter compartment after discharge.

CONCLUSIONS

The thin-film silver difluoride electrodes that were formed on a graphite substrate from the elemental constituents were electrochemically active. The electrochemical studies show that the method produces an electrode that can be discharged in a non-aqueous electrolyte with efficiencies greater than 70 percent. Because no attempt was made to charge the system, the applicability of these as secondary battery electrodes remains undetermined. The method should be applicable to other transition metals, and some preliminary data with copper indicate this to be true.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, September 15, 1972,
502-05.

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TABLE I. - GRAPHITE SUBSTRATE

Type	Description	Effect of fluorine exposure at 250° C (523 K)
Rod	High-density pyrolytic graphite 6.35 mm (1/4 in.) diam	Increased porosity and cracking
Sheet	Grafoil, 99.9% graphite 0.127 mm (0.005-in.) thick; Union Carbide G3503	No effect
Felt	Graphite felt 5.08 mm (0.2 in.) thick, Union Carbide X3101	Slight reaction on fiber ends

TABLE II. - COULOMBIC EFFICIENCY

Discharge current density, mA/cm ² (a)	Coulombs determined by -		Efficiency, percent
	Weight of reactant	Electro- chemical discharge	
3.2	119	95	80
10	230	161	70
25	244	190	78

^aGeometrical area, 1 cm².

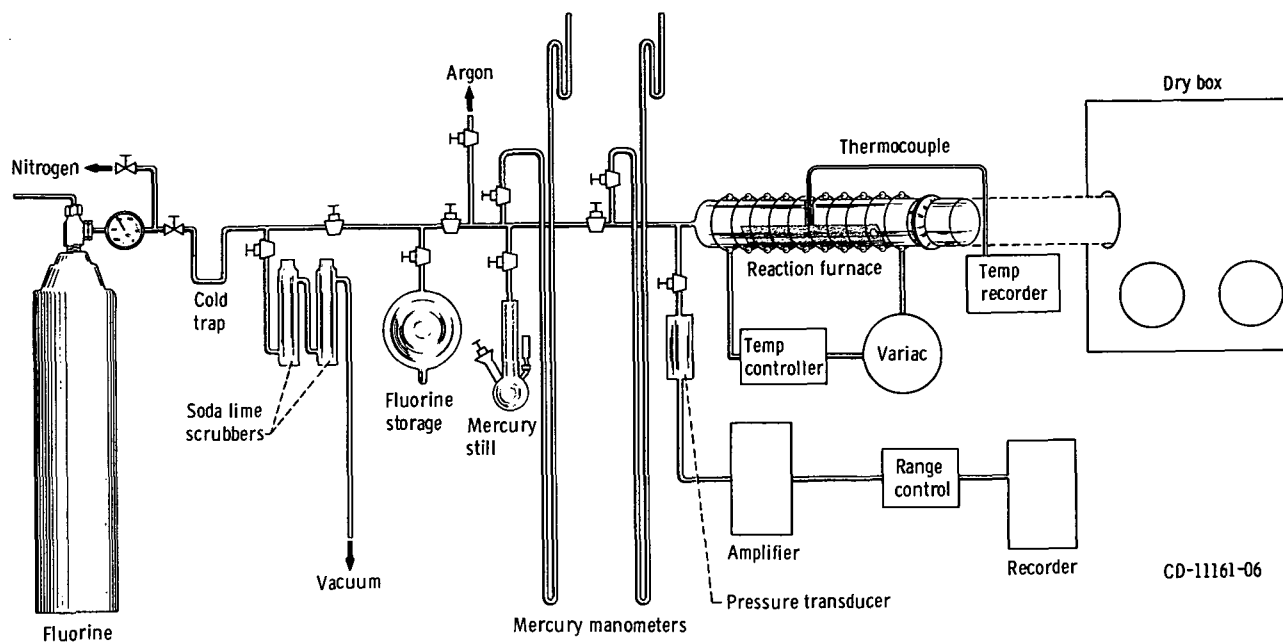


Figure 1. - Apparatus.

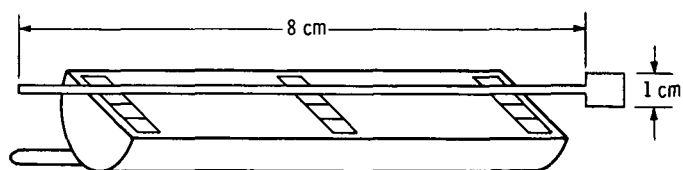


Figure 2. - Monel sample holder and sample.

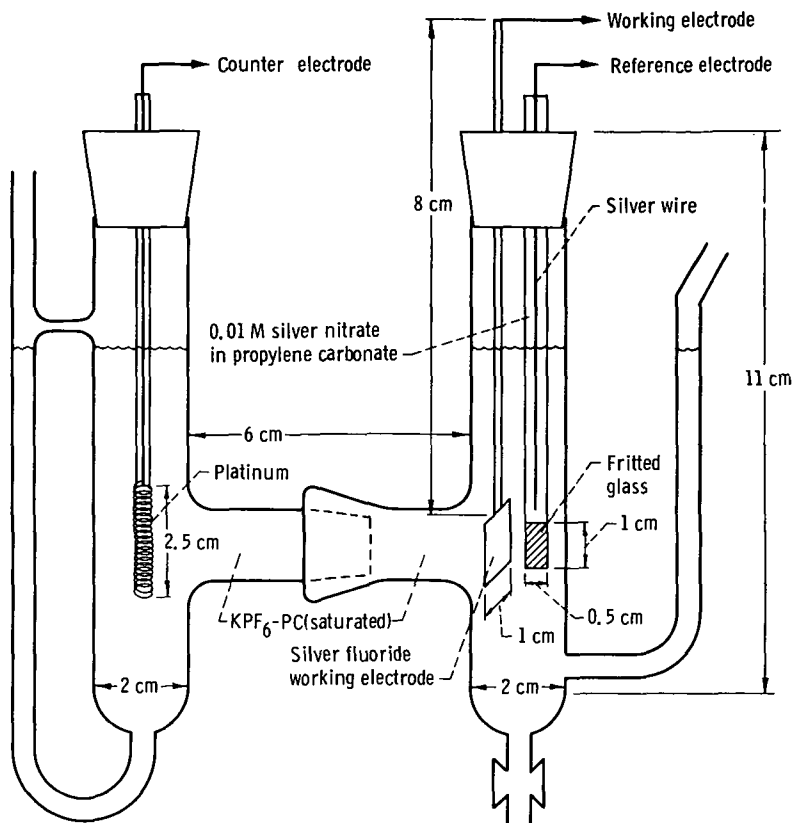


Figure 3. - Electrochemical cell.

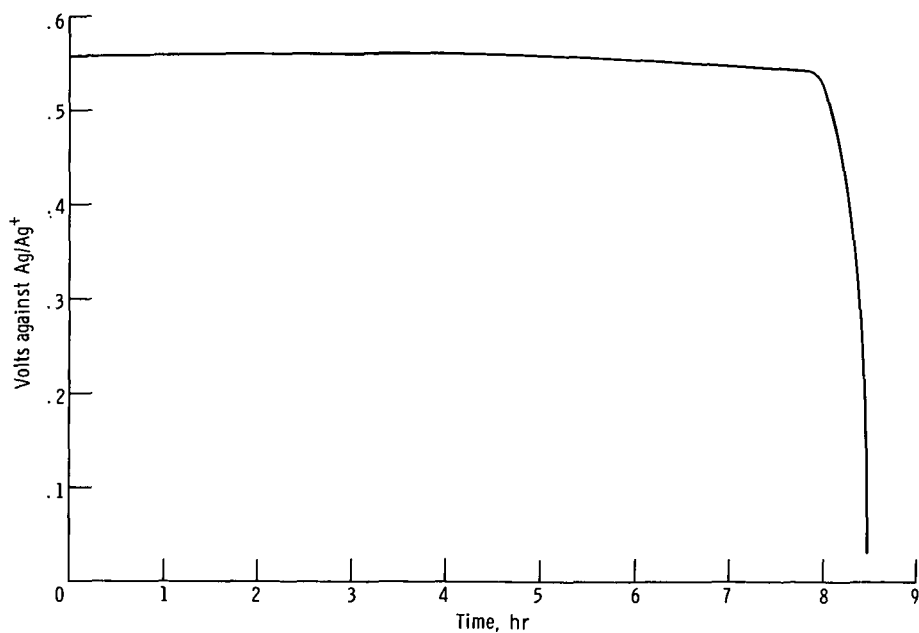


Figure 4. - Discharge profile for silver fluoride in saturated KPF₆ - PC at 3.2 milliamperes per square centimeter.



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